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A Field Intercomparison of Sulfate Dry Deposition Monitoring and Measurement Methods : Preliminary Results.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The Illinois State Water Survey hosted a three-week field intercomparison of several sulfate dry deposition measurement techniques during September 81. The site was an 80-acre grass field in a rural area 14 km southwest of Champaign, IL. The vegetation consisted of mixed grasses 25-35 cm high. The experimental techniques used were surrogate surfaces (plates, dishes, and buckets) and eddy correlation for particles containing sulfate. The eddy correlation data are not yet available, so this preliminary intercomparison is restricted to the surrogate surfaces, which were Teflon disks, polycarbonate dishes, Teflon-coated aluminum plates, and HASL dry buckets. Ambient particulate sulfate was determined from dichotomous filter samples; the mean sulfate concentration was 5.4 $\mu g/m^3$, with a range of 0.63 to 13.2 $\mu g/m^3$.

The sulfate dry flux ranged from 200-5000 $ng/m^2/min$ as measured by all of the techniques. However, large differences were found among the methods. The HASL dry bucket usually gave values of about twice the mean value, and the Teflon-coated aluminum plates about one-half the mean value. Considering all the techniques, the sulfate dry deposition velocity ranged from 0.15 to 0.91 cm/sec. Clearly, surrogate surface design and exposure procedure have a major influence on sulfate dry flux collected by the sampler.

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1. INTRODUCTION

The acidification of aquatic ecosystems in the northeastern U.S. and northern Europe has been a topic of intensive research and modeling efforts in recent years[1]. It is generally believed that this problem is a consequence of the transport, transformation, and deposition of acidic atmospheric pollutants, both gases and particles[2]. To determine accurately the mass of acidic species being transferred from the atmosphere to the surface, and to assess successfully the outcome of possible pollution control strategies, reliable knowledge of deposition rates is essential. Both wet and dry deposition processes contribute significantly to the total loadings of acidic materials. For dry deposition, though, the uncertainties associated with mass transfer estimates are probably at least one order of magnitude. This causes unacceptably large uncertainties in computations that rely on estimates of dry depostion. Not only determinations of total acidic loadings, but also model-derived predictions for the outcomes of alternative pollution control strategies have remained very uncertain.

Refinement in the ability to measure and monitor dry deposition of atmospheric gases and particles, then, has also been the object of much recent research effort. Approaches to the problem can cover a wide range of temporal and spatial scales. Mass-balance studies of pollutant accumulation can involve large areas and long periods of time, often

years. Laboratory studies, for example wind-tunnel investigations of deposition rates, seek to improve understanding of specific details of the very complex deposition process. In the field, however, techniques used to measure deposition can be thought of within two broad categories. First, flux monitoring techniques estimate deposition by the measurement of the rates at which pollutants accumulate on surfaces or within collectors of various designs. Some of these methods are also referred to as surrogate-surface monitoring. The second broad category is the flux parameterization approach, in which the effects of the surface, the atmosphere, and each pollutant's chemical and physical properties are studied in relation to vertical flux rates in the near-surface atmospheric layer. This category includes techniques such as gradient measurements, eddy correlation, and the variance method. Accurate measurement of dry deposition is an important facet in the understanding of the transport, transformation, and fate of atmospheric pollutants. Yet, no consensus has been reached on a reliable and practical method by which to routinely monitor dry deposition rates[3]. This intercomparison of dry deposition monitoring and measurement methods was an approach to verification or calibration of depostion estimates from the various methods now available.

2. EXPERIMENTAL

2.1 Sampling period and field site description.

As an effort towards reduction of the uncertainty in the knowledge of dry deposition rates, the Illinois State Water Survey (ISWS), with support from the US Environmental Protection Agency (USEPA), hosted a field intercomparison of several sulfate deposition methods during September, 1981. The intercomparison reported here was a pilot experiment, limited in duration to about three weeks and limited in scope to five methods, with the measurement of sulfate deposition rate being a common parameter. The site of the intercomparison was Monticello Road Field Site (MRFS), an 80 acre grass field in a rural area 14 km southwest of Champaign, Illinois. Vegetation on MRFS during the 4 to 25 September sampling period consisted of mixed grasses 25 to 35 cm high, with some patches of taller weeds. The surrounding farm fields were generally planted in corn, about 200 cm high, with a small area of soybeans, about 80 cm high, bordering the south end of MRFS. The array of dry deposition monitors and measurement experiments was set up near the center of the site, within an area of uniform vegetation. Figures 1a and 1b are plan views of MRFS and the array of samplers used in the pilot study. The various experiments were set up with sufficient spacing between collectors to avoid obstruction of prevailing wind flow. Further, all servicing of the collectors and instruments was coordinated between experimenters so as not to contaminate ongoing samples. Some

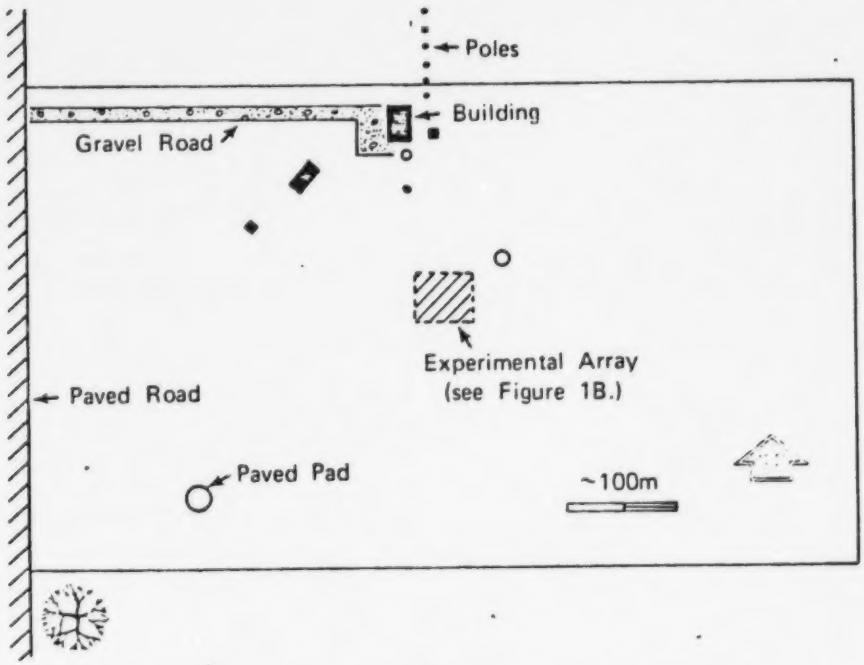

Figure 1A. Plan view of Monticello Road Field Site.

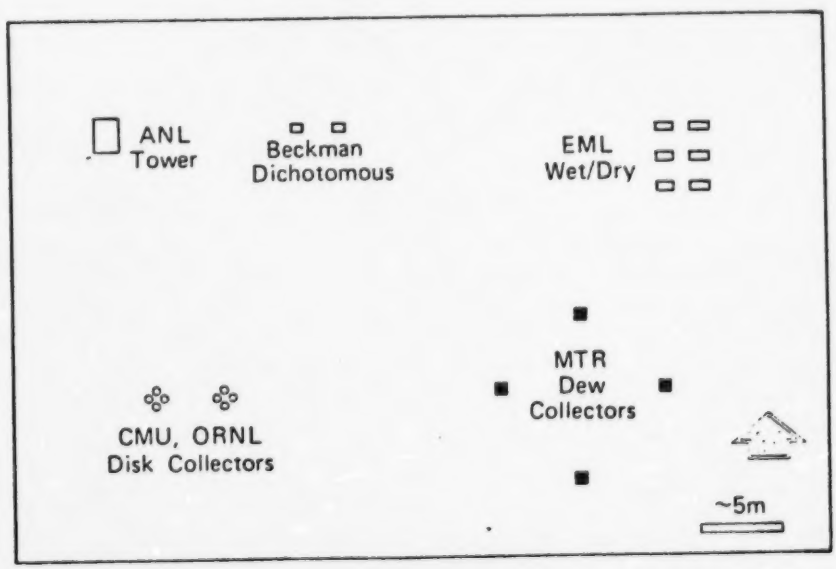

Figure 1B. Plan view of dry deposition monitoring equipment.

periods of winds in the 285° through 075° sector made data collection by some methods difficult due to the presence of obstructions to ambient wind flow from the north sector. Also, periods of sporadic light rain occurred on September 14 (Julian Date 257) and 16 (JD 259). This hampered some sample collection efforts.

2.2 Deposition measurement methods.

Experimentation during the pilot study was conducted with the objective of determining sulfate flux by several different methods at a common site, while sampling concurrently if possible. However, sampling criteria and protocols usually employed in the application of each method were followed. For example, it should be noted that not all surrogate surfaces were mounted at the same height above ground or exposed in a similar manner. Carnegie-Mellon University (CMU) deployed two types of flat Teflon plates; both were disks about 10 cm in diameter, but one type had a rim about 3 mm high, while the other type was rimless. Oak Ridge National Laboratory (ORNL) used 9.5 cm diameter polycarbonate petri dishes as surrogate surface collectors. These dishes had 15 mm high rims. Both the CMU disks and the ORNL dishes were exposed at 40 cm above ground, in an area where the vegetation was uniformly 25 to 35 cm high. Exposure times for both types of surfaces were from 2900 to 4800 minutes, and most samples were collected concurrently to maximize intercomparibility. Exposure was done by mounting the plates at the sampling height, with the collection surface

horizontal and facing upwards. Disks and dishes were left exposed, during periods of no rain, for as many days as possible. Samples were collected when rain was imminent or threatening. The CMU disks were extracted at the field site by rolling two successive ~1 ml drops of distilled deionized water across the collection surface. Each drop was allowed to contact all of the collection surface, by keeping the drop in motion for about 60 seconds. After extraction, the disks were thoroughly cleaned and reused for the next exposure. After exposure, the ORNL dishes were tightly covered, sealed in polyethylene bags, and transported to the ISWS laboratory. In the laboratory, the dishes were extracted with 30 ml of distilled deionized water. The water was magnetically stirred for 30 minutes with just enough speed to keep the solution in circular motion. This avoided splash-out and evaporative sample loss problems, while insuring complete sulfate recovery[4]. The ORNL dishes were not reused; a new, pre-cleaned dish was set out for each sample. The MITRE Corporation (MTR) collected dry deposition and dew on 76 cm by 76 cm square flat plates constructed of thin Teflon sheets laminated to aluminum. The MTR plates were exposed 1 m above ground, about 10 m from the CMU and ORNL collectors. Exposure periods ranged from 700 to 4320 minutes. The sample collection criteria for the MTR plates was somewhat different, however, which prevented concurrent sampling with CMU and ORNL. The MTR collection procedure was to clean the plate *in situ* at the beginning of each sample period, and collect the deposited material by squeegeeing off the accumulated dew early in the morning. This is in contrast to the CMU and ORNL plates, which were always dry when exposures were ended. Thus, no additional water was

added to the MTR samples, and liquid sample volume was dictated by dewfall volume. The Department of Energy / Environmental Measurements Laboratory (EML) set up six wet/dry bucket collectors,three HASL-type and three manufactured by Aerochemetrics, Incorporated. The dry buckets, open to the atmosphere during periods of no rain at 1.5 m above ground, were sealed on the collector and changed generally at 1440 minute intervals. For every exposure period, all six buckets were changed at the same time, yielding six replicate measurements by this technique. The sealed buckets were returned to EML at the end of sampling for extraction and analysis. The wet-side buckets were collected once, at the end of the pilot study period.

In order to intercalibrate the analysis of samples for sulfate between the participating laboratories, a series of sulfate solutions of known concentrations were generated at the ISWS laboratory. These were sent as a series of blind samples to each participant performing sulfate analyses in the pilot study. All sulfate analyses reported here were performed by ion chromatography, except for the ORNL samples, which were analyzed by automated colorimetry. The four (EML, MTR, ORNL, CMU) sets of results agree very well with one another and with the values specified for the known solutions. Table 1 is a brief compilation of the results of this limited interlaboratory check. The five percent overall mean difference is a very small source of variability in the intercomparison, compared to the much larger variability in sulfate fluxes determined by the various deposition collectors. The sulfate

Table 1. Results of Pilot Study Interlaboratory Sulfate Analysis Check ($SO_4^=$, $mg\text{-}l^{-1}$)

STANDARD CONCENTRATION	MTR	EML	ORL	CMU	FOUR-LAB MEAN
blank	.07	.062	<0.2	.048	--
2.0	2.05	2.19	1.98	1.89	2.03
4.0	4.13	3.92	4.05	4.02	4.03
10.0	10.06	10.25	10.57	9.87	10.19
14.0	13.59	14.38	15.67	14.80	14.61
20.0	19.57	20.64	21.50	21.68	20.84

results from each participant are therefore used without correction factors of any kind in the intercomparison.

Argonne National Laboratory (ANL) used fast-response micrometeorological sensors and a flame - photometric sulfate detection system to conduct eddy correlation measurements of sulfate flux. The instruments were located 6 m above ground on an 8 m aluminum scaffolding tower. The data were recorded on magnetic tape, and later analyzed at ANL. Ambient meteorological conditions (temperature, dew point, wind speed and direction) were also monitored by ANL during the first two weeks of the pilot study. Additional meteorological data were obtained from records of surface observations made at Willard airport, 4 km northeast of MRFS.

Determinations of ambient particulate sulfate concentrations were made in several ways during the pilot study. First, CMU used 0.2 μm Teflon filters , 47 mm diameter, with 4.9 and 10.0 liter min^{-1} flow restricting orifices. Pairs of these filters, in stainless steel holders, were exposed at 0.5 and 8.0 m above ground, for periods of 116 to 1440 minutes. The filters were extracted by immersion and manual agitation in 5 ml distilled deionized water for 3 minutes. The filters were then washed by an additional period of agitation in water, and reused. The 5 ml extracts were placed in polyethylene bottles and returned to CMU for analysis. Second, ISWS operated two circular

streaker samplers, with one-week duration 0.4 μm Nuclepore filters, continuously during the first two weeks of the pilot study. The streaker samplers were operated from a single, high-capacity vacuum pump, at a flow rate of 0.8 liter min^{-1}. The samplers were located at the 0.5 and 8.0 m levels, near the CMU filter holders. The two pairs of CMU filters were also operated from a common vacuum pump. At intervals throughout the pilot study, the sampler positions were interchanged so that variations due to sampler differences would be apparent. It was intended that vertical gradients in sulfate (and other elemental) concentrations would be measured across the 0.5 to 8.0 m height difference. Part of the streaker data was lost due to a Proton Induced X-ray Emission (PIXE) analytical problem, and a high degree of variablility occurred in the CMU filter results, probably due to extraction problems. This made the determination of vertical concentration gradients very difficult; however, the data from these samples can be used to evaluate ambient particulate sulfate and other elemental concentrations. Finally, ISWS operated two Beckman automated dichotomous samplers, on loan from USEPA, with type 505 Teflon filters. Samples were collected at 16.7 liter min^{-1} for periods of 150 to 1660 minutes, throughout the pilot study period. The dichotomous sampler filters were extracted at USEPA and analyzed for sulfate.

3. RESULTS

3.1 Preliminary Nature of These Results.

The data reported here are an as yet partial set of the results of the pilot intercomparison. The results from some experiments are not available, others are incomplete, and all must be considered as "first-look" tabulations of the September, 1981 samples. Due to the small number of samples, no statistically significant differences between fluxes determined by the rimmed and rimless CMU Teflon disks could be found. Thus, the reported sulfate fluxes are mean values from both types of disk. The ORNL flux values are means of from two to four samples, depending on how many concurrent samples were exposed during a given period. Sulfate fluxes for the MTR plates are given only for the shortest, usually overnight, sample exposures. This is due to anomolous, and as yet poorly understood, results for some of the MTR plates exposed more than 1440 minutes. Some of the 6 concurrent EML dry bucket measurements are missing , for some exposure periods. In the case of less than six values having been reported for a given period, the EML flux reported is the mean of all the values which were available. The missing data are apparent outliers that, again, are as yet not fully interpreted. Because of the missing and incomplete data, no discussion of variability associated with the mean fluxes reported for each method has been attempted. Interpretation of the ANL eddy correlation data was not yet available, which limits the scope of the

results reported here to the four surrogate surface techniques: CMU - Teflon disk, ORNL - polycarbonate dish, MTR - Teflon / aluminum plate, and EML wet/dry dry-side buckets.

3.2 Ambient Sulfate Concentrations.

The ambient particulate sulfate results used here are from filters exposed in the Beckman dichotomous samplers only. The fine and coarse concentrations were summed, and mean total sulfate values for concurrently exposed samples from both samplers are reported. Table 2 is a compilation of the sampling period mean sulfate concentrations. The mean sulfate concentration for the entire pilot study period was about 5.4 $\mu g\ m^{-3}$, with a maximum of 13.23 $\mu g\ m^{-3}$ on JD 256, and the minimum of 0.63 $\mu g\ m^{-3}$ on JD 260. The periods of minimum sulfate concentration correlate well with periods when sporadic light rain showers occurred at or near MRFS. Sulfate maximums occurred with persistent west and southwest winds. From these data, daily average sulfate concentration for each midnight to midnight period were calculated, and plotted in Figure 2 Where several exposure periods, i.e. different filters, overlapped a day, time - weighted average concentrations were computed. The CMU filter samples and ISWS streaker sulfur concentrations generally follow trends in the dichotomous filter data, but do not cover the entire sampling period.

Table 2. Ambient Sulfate concentration ($\mu g\ m^{-3}$) during September, 1981

Sample times Julian Date (GMT on-off)	Concentration	Sample times Julian Date (GMT on-off)	Concentration
248 (0000-2359)	5.23	257 (0000-1200)	11.96
249 (0000-2359)	8.61	257 (1210)-258(1500)	1.06
250 (0000-2359)	11.90	258 (1500-2359)	4.73
251 (0000-2359)	2.83	259 (0000-1200)	3.74
252 (0000-1420)	2.19	259 (1210-2359)	1.68
252 (1430-2359)	1.83	260 (0300-0800)	0.63
253 (0000-1200)	3.67	260 (1200-2359)	1.25
253 (1210-1800)	8.50	261 (0000-1200)	1.20
253 (1830-2359)	5.81	261 (1400)-262(1400)	1.71
254 (0000-1200)	7.20	262 (1410)-263(1400)	2.75
254 (1210-2359)	7.90	263 (1410)-264(1400)	4.49
255 (0000-1200)	8.67	263 (1410)-265(1400)	5.10
255 (1210-2359)	9.81	265 (1410)-266(1400)	3.77
256 (0000-1200)	10.66	266 (1410)-267(1800)	3.65
256 (1210-2359)	13.23		

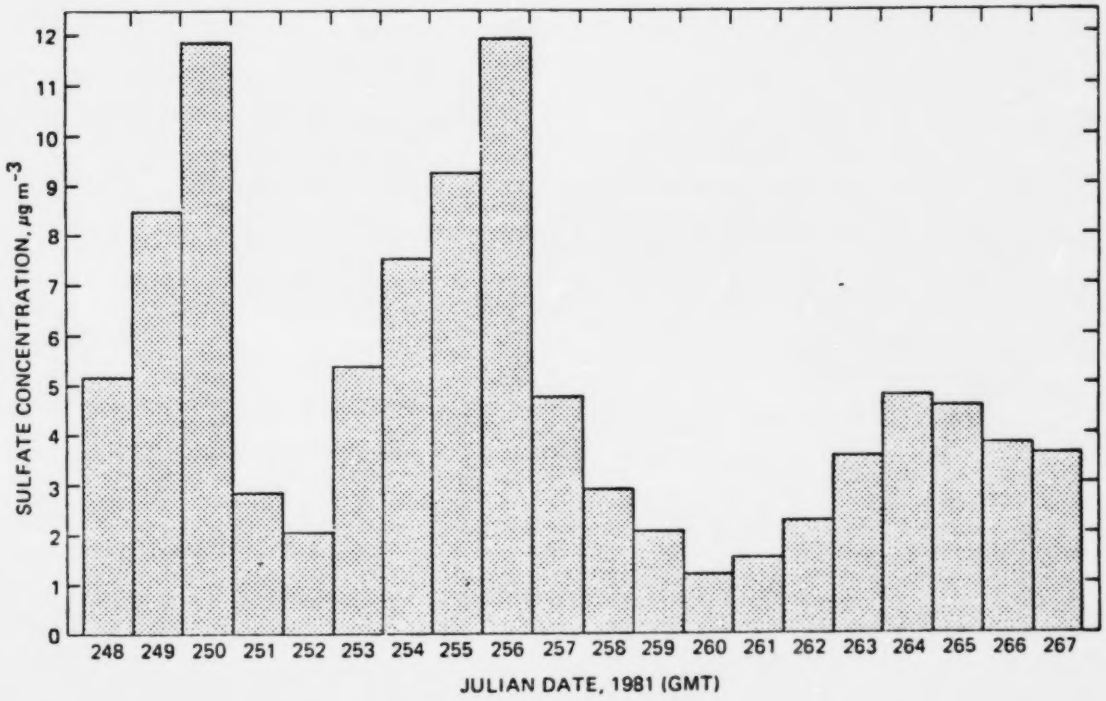

Figure 2. Ambient particulate sulfate concentration during the pilot study period.

3.3 Sulfate Flux Intercomparison.

The mean sulfate dry deposition fluxes for the four surrogate surface methods used in the pilot study are shown in Figure 3. It is readily apparent that, for any given period of time, differences of from a factor of two up to nearly an order of magnitude exist in the results from the four types of collectors. The flat-plate collectors, MTR Teflon on aluminum plates and CMU Teflon disks, consistently reported the lowest sulfate fluxes. The ORNL polycarbonate petri dishes measured fluxes slightly greater, and the EML dry-side buckets gave consistently the highest values. This ranking holds true across the range of ambient particulate concentrations encountered during the month (Figure 2).

In order to quantify the general result described in Figure 3, the reported flux values for each method were converted into daily - average fluxes, corresponding to midnight to midnight periods. Where several values overlapped a day, time - weighted averages were used. A single sample which covered at least 14 hours, i.e. about 60 percent, of a day was used as the flux value for the entire day in this calculation. The daily - averaged fluxes derived in this way are given in Table 3. To compensate for the fact that all flux samples were not collected concurrently, daily mean ambient sulfate concentrations were used in computing deposition velocities (V_d) only when the dichotomous filter sample and the flux sample endpoints were within two hours of one

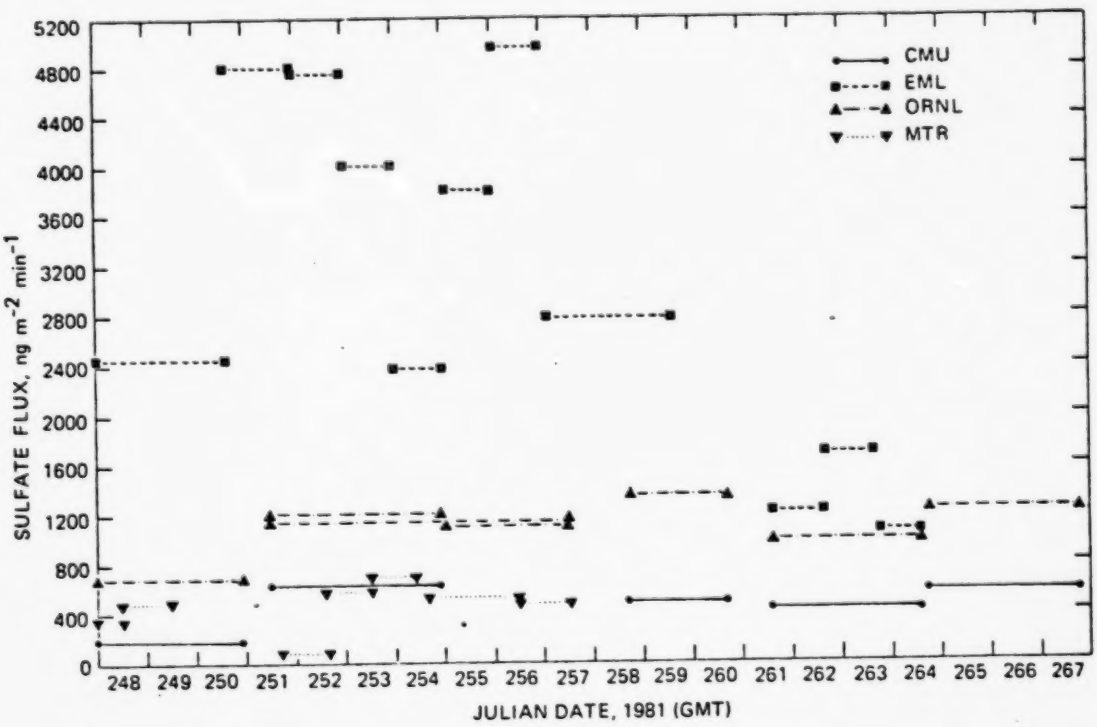

Figure 3. Mean sulfate flux determined by four monitoring methods.

Table 3. Derived daily mean Sulfate flux, (ng m^{-2} min^{-1}) and deposition velocity, V_d, (cm s^{-1}) for September, 1981

Julian Date, 1981	MTR Flux	MTR V_d	EML Flux	EML V_d	CMU Flux	CMU V_d	ORNL Flux	ORNL V_d
248	415	.133	2444	.518	194	.038	700	.137
249	480	.094	2444	.518	194	.038	700	.137
250			3622	.508	194	.038	700	.137
251			4800	1.37				
252	102	.076	4719*	3.87*	607	.203	1200	.401
253	587	.358	4041	1.25	607	.203	1200	.401
254	670	.154	2353	.517	607	.203	1200	.401
255	540	.097	3817	.688			1140	.176
206	535	.075	4970	.697			1140	.176
257	530	.188	2743	1.22			1140	.176
258			1743	1.22				
259			2743	1.22	517	.292	1350	.763
260					517	.292	1350	.763
261			1221	1.20				
262			1221	1.20	414	.232	1000	.561
263			1739	1.07	414	.232	1000	.561
284			1088	.405	480	.167	1100	.382
265					573	.240	1240	.518
266					573	.240	1240	.518
267					573	.240	1240	.518
$\bar{V}_d$	.147 $\pm$.088(8)		.907 $\pm$.345(15)		.190 $\pm$.085(14)		.356 $\pm$.186(17)	

* This value excluded from V_d mean calculation.

another. Otherwise, partial, time - weighted combinations of several dichotomous filter samples were used to compute a mean sulfate concentration for the flux - measurement period. Thus, the deposition velocities given in Table 3 are a good way to intercompare the daily results from the various flux monitors. Again, the graphically evident differences are clearly demonstrated. The mean V_d values are shown at the bottom of Table 3 with standard deviations and the number of daily - average fluxes available. The mean V_d values are means of all values computed for each method. Comparing more directly, by considering only the days when several methods reported results, does not alter the trend or magnitude of the differences indicated by overall means. The ORNL petri dishes determined a sulfate V_d value about two times as great as the V_d from the CMU and MTR methods. The EML dry-side buckets give values about five times higher than the CMU and MTR methods. Surrogate surface design, including collector geometry, material, and exposure technique clearly has a major influence on the sulfate deposition measured by the collector.

4. ACKNOWLEDGEMENTS

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